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Archives of Applied Science Research, 2015, 7 (1):42-47
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Na₂Ti₆O₁₃ belts: A comparative study on structural, optical and morphological properties prepared by sol-gel and solid state reaction routes

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ABSTRACT

In this paper sodium hexatitanate (Na₂Ti₆O₁₃) belts were prepared by two specific synthesis process such as sol-gel and solid state reaction methods. The structural, morphological and optical characteristics were performed by XRD, SEM and UV-vis absorption spectroscopy. The crystallite size and unit cell volume of sodium hexatitanates (Na₂Ti₆O₁₃) synthesized by sol-gel method have less than same obtained by solid state reaction method. The energy band gap (3.18eV) of Na₂Ti₆O₁₃ prepared by sol-gel method was obtained larger than (3.07eV), prepared by solid state reaction method. Beyond it, Na₂Ti₆O₁₃ was tested as photocatalyst on the degradation of methyl orange under visible light and obtained better activity for the sample synthesized by sol-gel reaction route. From the observed data we have concluded that the sodium hexatitanate (Na₂Ti₆O₁₃) whiskers synthesized by sol-gel method showed superior properties than the solid state reaction method.

Keywords: Sodium hexatitanate (Na₂Ti₆O₁₃), Sol-gel method, Solid state reaction route, Energy band gap, Photocatalyst XRD, SEM.

INTRODUCTION

In recent years, alkali titanates are the derivative of titania or titanium dioxide (TiO₂) which is a newly synthesized compound in chemical world. The general formula of alkali titanate is A₂Ti_nO_{2n+1} (where A = Li, Na and K etc and n = 2-8) [1-2]. Alkali titanates are well known functional materials because of their outstanding electronic, magnetic, optical, catalytic, mechanical properties and thermal stability. Among all, titanates are of great interest in many important applications such as ion exchange, photoluminescence[3], photochemical catalyst, RuO₂-supporting Na₂Ti₆O₁₃ show high photocatalytic activities for water decomposition [4-6], filter materials, reinforced materials, acoustic absorbing materials and as well as heat insulator[7]. It has also been reported that Na₂Ti₆O₁₃ have various interesting technological applications such as ceramic capacitors, dielectric sensors, biosensors [8-9]. These properties and applications are related to the morphology, size and crystallinity of alkali titanates. In order to improve the functional properties such as photocatalytic activities or ion exchange ability, it is highly desirable to control the size and morphology of the titanates[10]. Alkali titanates are comparatively cheap fibrous materials which have high thermal durability, chemical resistivity and dispersibility. All these properties make them useful as reinforced materials, heat insulating paints, automotive brake linings and photocatalytic materials [5, 11-19]

Sodium hexatitanates could be synthesized by sol-gel method, molten salt calcinations routes, novel hydrothermal process and solid state reaction methods in molar ratio. In this study nano sodium hexatitanates ($\text{Na}_2\text{Ti}_6\text{O}_{13}$) were successfully prepared by sol-gel and solid state reaction methods. Besides these properties the photocatalytic degradation of methyl orange under visible light at room temperature was also tested for both the samples. The comparative studies were done on structural, optical and morphological behavior of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ synthesized by two different methods.

MATERIALS AND METHODS

2.1 Synthesis-

The compound $\text{Na}_2\text{Ti}_6\text{O}_{13}$ was prepared by sol-gel method using titanium (IV) isopropoxide, sodium acetate, ethanol and distilled water. In this method, an adequate stoichiometric amount of titanium isopropoxide was placed into a 500 ml round bottom flask. Sodium acetate was dissolved in 20 ml of distilled water and ethanol, and then added drop by drop into the flask containing the titanium isopropoxide. The mixture was heated under reflux at 70 °C during 72 h under constant stirring. Basic pH of the solution was set and controlled by using small amount of NH_4OH . After heating, the solution was aged at 25 °C for 24 h until the gel formation. The gel was heat treated at different temperature ($T=1000$ °C) for 8 h in an electric furnace.

In typical solid state reaction method sodium hexatitanate belts were synthesized by mixing adequate stoichiometric amounts of Na_2CO_3 and TiO_2 powder with acetone in mortar and grinded for 1 hour. After mixing, the mixture was placed in an alumina crucible and calcinated at 1000 °C for 12 h in an electric furnace.

2.2 Characterization-

(i) XRD-

Structural properties of sodium hexatitanates belts ($\text{Na}_2\text{Ti}_6\text{O}_{13}$) synthesized by sol-gel and solid state reaction methods were determined by X-ray diffraction (XRD) using Rigaku-miniflex. X-ray diffractometer with $\text{Cu-K}\alpha$ radiations ($\lambda = 0.15406$ nm) in 2θ range from 10° to 70° with scan rate at $2^\circ/\text{min}$ at room temperature. Lattice parameters were calculated by applying the equation:

$$\frac{1}{d^2} = \frac{h^2}{a^2 \sin^2 \beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2 \sin^2 \beta} - \frac{2hl \cos \beta}{ac \sin^2 \beta} \quad (1)$$

(ii) UV-vis absorption Spectroscopy-

UV-vis absorption spectra for the samples were taken by Perkin Elmer Lambda 35 UV-visible spectrometer. The energy band gap was calculated by using Tauc relationship:

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2)$$

For alkali titanates nanoparticles the absorbance coefficient α obey the above relation with $n = \frac{1}{2}$ (for direct allowed band gap semiconductor). The photocatalytic tests were carried out by using aqueous solution of methyl orange (1.0×10^{-5} M) under irradiation of visible light. 0.02 gm $\text{Na}_2\text{Ti}_6\text{O}_{13}$ powders (synthesized by sol-gel and solid state methods) were weighted and used as photocatalysts. The photocatalyst and methyl orange suspension was kept under the irradiation of visible light at room temperature with continuous stirring. The characteristic absorption of methyl orange $\lambda = 464$ nm was chosen to observe the photocatalytic degradation process on UV-visible spectrometer by the exposure visible light with increase in irradiation time.

(iii) SEM-

Morphologies and microstructures of sodium hexatitanates belts ($\text{Na}_2\text{Ti}_6\text{O}_{13}$) were examined using scanning electron microscope (SEM, VEGA II LSU), operating at 30 kV.

RESULTS AND DISCUSSION

3.1 Structural Properties-

Fig. 1 shows the XRD patterns of sodium hexatitanate belts ($\text{Na}_2\text{Ti}_6\text{O}_{13}$) prepared by sol-gel and solid state reaction routes recorded at room temperature. The peak position of each sample exhibits the monoclinic structure and no other impurity peak was observed in XRD pattern which confirms the single phase formation. The lattice constants

were calculated from XRD pattern by using equation 1 and shown in table 1. The unit cell parameters also reported by S. Andersson *et al* [20].

Table 1 Lattice parameters and cell volume of $\text{Na}_2\text{Ti}_6\text{O}_{13}$

Sample	Lattice parameter a (Å)	Lattice parameter b (Å)	Lattice parameter c (Å)	β°	Unit cell volume (Å ³)
$\text{Na}_2\text{Ti}_6\text{O}_{13}$ (Sol-gel)	15.168	3.720	9.122	99.246	508.021
$\text{Na}_2\text{Ti}_6\text{O}_{13}$ (Solid state)	15.136	3.752	9.163	99.302	513.526

From table 1, it can be observed that sol-gel method shrink the unit cell volume as compare to solid state reaction route; this is because of small crystallite size in sol-gel formation.

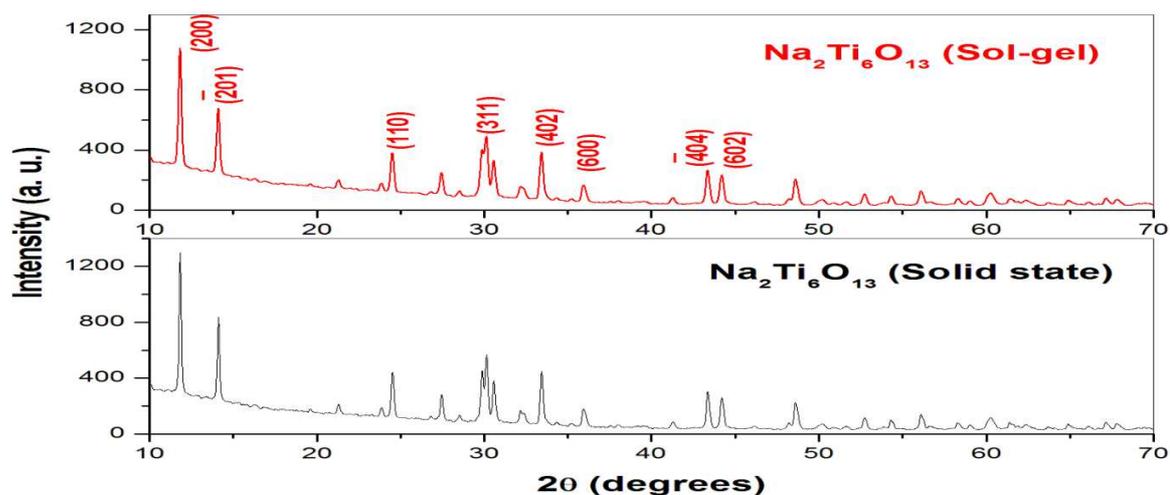


Fig. 1 XRD pattern of sodium hexatitanates ($\text{Na}_2\text{Ti}_6\text{O}_{13}$) synthesized by sol-gel and solid state

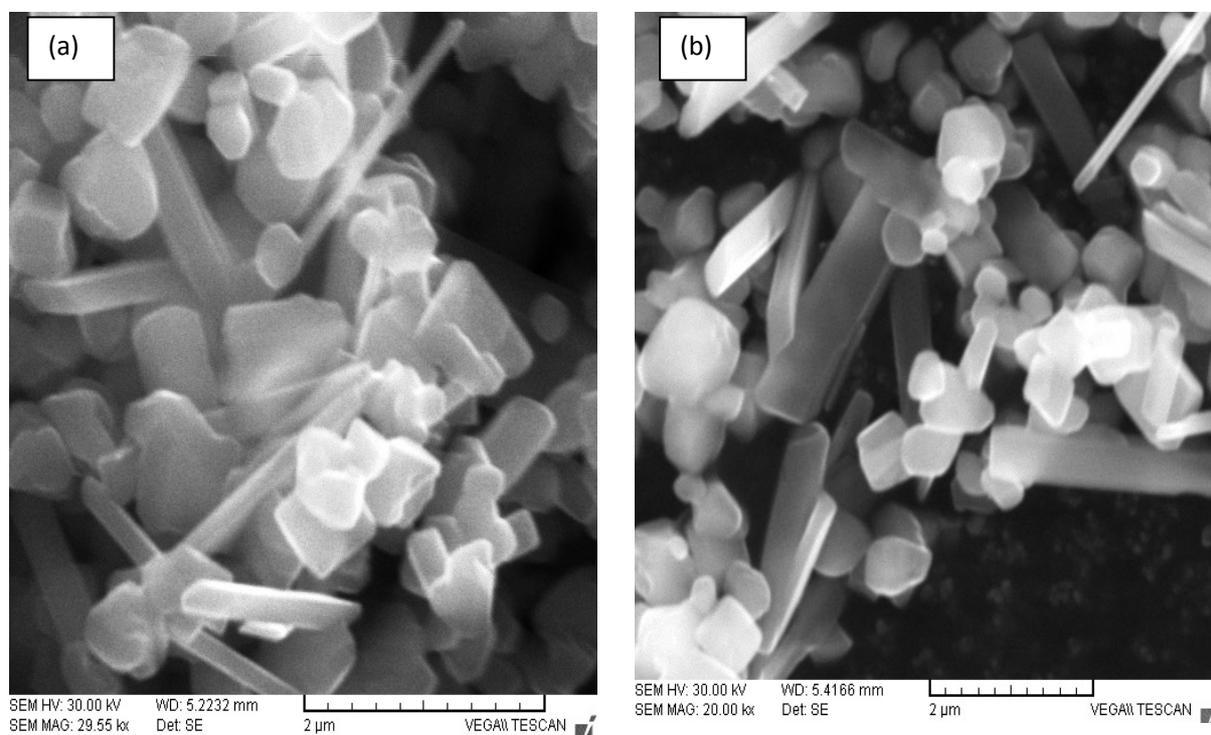


Fig. 2: Low magnification SEM image of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ prepared by sol-gel (a) and solid state reaction method (b) respectively

3.2 Morphological Properties-

The morphology of the sodium hexatitanates ($\text{Na}_2\text{Ti}_6\text{O}_{13}$) prepared by sol-gel method and solid state reaction route were characterized by scanning electron microscope (SEM) shown in Fig. 2. The fig. 2(a) represents the low magnification image of sodium hexatitanates synthesized by sol-gel showing nanobelts with cross sectional width less than 100 nm while fig. 2 (b) shows the low magnification of the same particles, have larger thickness of belts synthesized by solid state reaction method. This attributed that by using sol-gel method we can control the synthesis of particles with a particular shape and size.

3.3 Optical Properties-

UV-vis absorption spectrum of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ of nanobelts in order to obtain clues regarding the electronic structure, shown in fig. 3. The absorbance is expected to depend on several factors, such as band gap, surface roughness and impurity centers. The absorption spectrum obtained by sol-gel sample was shifted towards the shorter wavelength region. This effect might be due to the quantum size effect [21]. In order to calculate direct band gap Tauc relationship used [22].

$$\alpha h\nu = A(h\nu - E_g)^n$$

Where A is a constant that depends on the properties of material, α is the absorption coefficient given by $\alpha = 2.303$ (Ab/t), where, Ab is absorbance and t is the cuvette thickness (1 cm in present case), $h\nu$ is the photonic energy, E_g is the energy band gap. n has different values depends on electronic transition types, for a allowed direct transition $n = 1/2$, a forbidden direct transition $n = 3/2$, a allowed indirect transition $n = 2$ and for a forbidden indirect transition $n = 3$ [23-24]. The plots of $(\alpha h\nu)^2$ versus $h\nu$ for $\text{Na}_2\text{Ti}_6\text{O}_{13}$ samples are shown in Fig.3 (a) and Fig. 3 (b).

The Tauc relationship was used to calculate the direct allowed band gap for the samples of sodium hexatitanates ($\text{Na}_2\text{Ti}_6\text{O}_{13}$) nanobelts synthesized by sol-gel and solid state reaction methods. The measured band gap was found to be 3.18 eV for sodium hexatitanates synthesized by sol-gel, which is higher than the value 3.07 eV found for the same, synthesized by solid state reaction method. This can be incriminated due to the quantum confinement effect of nanoparticles [25]. This result agrees with the previously reported [26].

3.4 Photocatalytic Test-

In this experiment photocatalytic activity of prepared sodium hexatitanate ($\text{Na}_2\text{Ti}_6\text{O}_{13}$) by two different methods were tested by the degradation of methyl orange under visible light irradiation. It was evaluated by measuring the photodegradation of a solution of methyl orange (1.0×10^{-5} M, 400 ml in a quartz vessel) in the presence of 0.02 gm $\text{Na}_2\text{Ti}_6\text{O}_{13}$ powder which was exposed to visible light at room temperature. Fig. 4 shows the absorbance decay with time 0 to 1 hour regarding the progress of the reaction with stirring the suspension. The color of the suspension faded simultaneously with an increase in irradiation time. Lastly the suspension of methyl orange changed from orange color to approximately colorless. Hence, the absorption peak value at $\lambda = 464$ nm decreases sharply as the visible light exposure time increases. The color of methyl orange solution remains unchanged when no $\text{Na}_2\text{Ti}_6\text{O}_{13}$ powder were added in visible light irradiation. Thus sodium hexatitanate ($\text{Na}_2\text{Ti}_6\text{O}_{13}$) act as affective photocatalytic material and degrade the methyl orange molecule into several different smaller molecules. In this work sodium hexatitanate ($\text{Na}_2\text{Ti}_6\text{O}_{13}$) with a rectangular tunnel structure has high efficiency to produce photoexcited charges (electron and holes) [6], which are thought to be associated with its high photocatalytic activity. Accordingly it has been observed from Fig. 4. that the phtocatalytic ability were found to be better for the $\text{Na}_2\text{Ti}_6\text{O}_{13}$ prepared by sol-gel method as compare to the same, prepared by solid state reaction route because the larger surface area or smaller particle size obtained in sol-gel method of preparation.

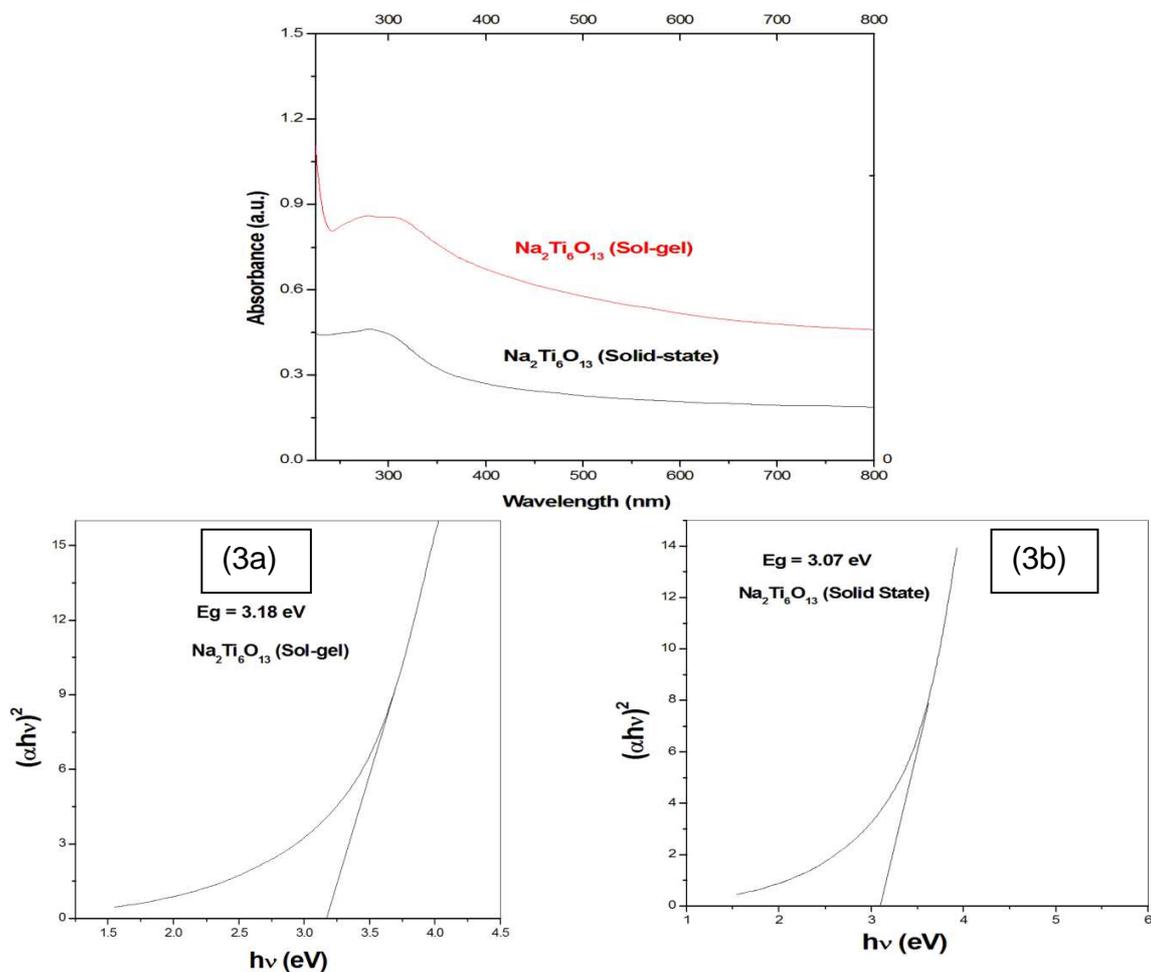


Fig. 3 : UV-vis absorption spectrum for sodium hexatitanates ($\text{Na}_2\text{Ti}_6\text{O}_{13}$). (a & b): Plots of $(\alpha h\nu)^2$ versus $h\nu$ for both the specimen.

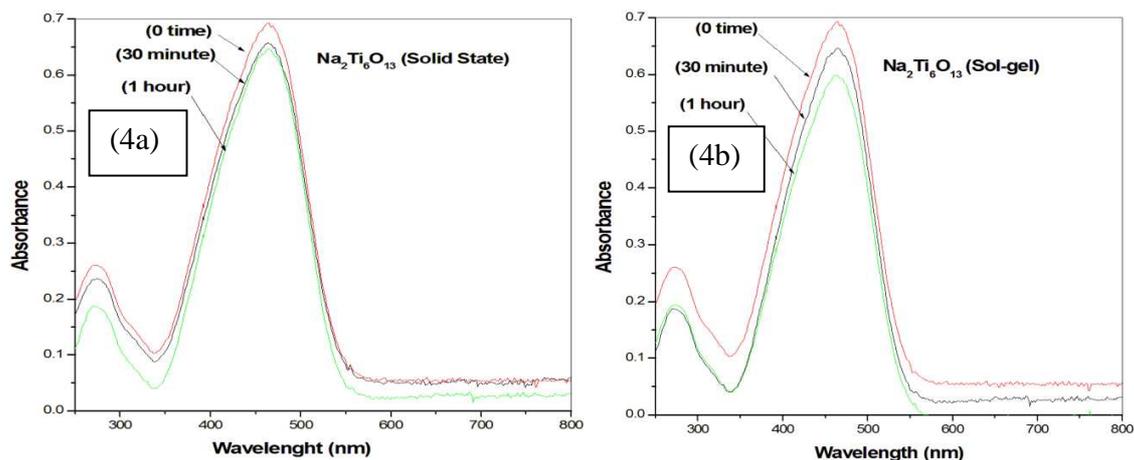


Fig. 4: Absorbance spectra of methyl orange solution (1.0×10^{-5} M, 400 ml) in the presence of 0.02 gm of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ nanobelts prepared by (a) solid state and (b) sol-gel reaction routes under the exposure of visible light

CONCLUSION

Sodium hexatitanate ($\text{Na}_2\text{Ti}_6\text{O}_{13}$) has been prepared successfully as a single phase by sol-gel and as well as by solid state reaction routes. Its crystal structure coincides to a monoclinic as confirmed by XRD pattern. Surface morphology was studied by scanning electron microscope (SEM) of single phase and exposed as nanobelts. The optical investigations have been carried out using optical absorbance. The optical band gap of the samples were measured from the Tauc relationship and observed that energy band gap increases with the decrease in particle size. $\text{Na}_2\text{Ti}_6\text{O}_{13}$ was tested as photocatalyst on the degradation of methyl orange under visible light and better results were found for the sample prepared by sol-gel than the same prepared by solid state reaction routes.

Acknowledgements

Authors are thankful to Integral University and Centre of Excellence in Material Science (Nanomaterials), AMU, Aligarh for providing infrastructure for the experiments carried out for the research.

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